

PATENT SPECIFICATION

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 D1Q1B2 D1Q1B3 D1Q2A1 D1Q2A2 D1Q3

C2B 1

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 SCHELLEKENS



(54) SPECTRAL SENSITIZATION OF PHOTOCONDUCTIVE COMPOSITIONS

(71) We, AGFA-GEVAERT (formerly Gevaert-Agfa NV), a Naamloze Vennootschap organised under the laws of Belgium, of 27 Septestraat, 2510 Mortsel, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to cyanine dyes and merocyanine dyes, and to their use for the spectral sensitization of photoconductive recording materials.

Photoconductive coatings containing a finely divided photoconductive substance e.g. photoconductive zinc oxide dispersed in a binder, are well known.

As described in United States Patent Specification 3,128,179 photoconductive zinc oxide can be sensitized with various organic dyes, e.g. Rose Bengal. A particular class of sensitizing agents proposed in this patent includes dyes known in the art of simple cyanine dyes, carbocyanine dyes and dicarbocyanine dyes comprising at least one carboxy group.

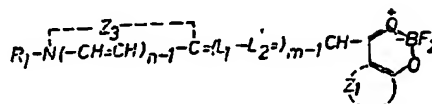
The dyes proposed in the above patent can be used for the spectral sensitization of photoconductive zinc oxide coated on a support from a homogeneous dispersion in a solution of an insulating binder in water or in an organic solvent. In practice however, they are only of very limited use because of their low fastness to light.

In accordance with the present invention new cyanine and merocyanine dyes are provided for the spectral sensitization of photoconductive substances such as photoconductive zinc oxide.

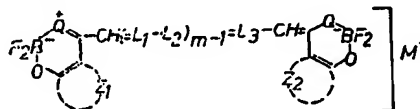
The present invention provides more particularly novel cyanine dyes corresponding to the formula I or II:

[Price 25p]

I.



II.



wherein:

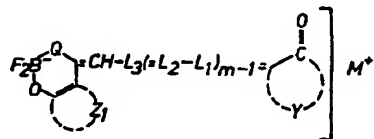
- Q stands for oxygen or the group N—R 45
 wherein R is an aliphatic cycloaliphatic or aromatic group, e.g. alkyl, aralkyl, cycloalkyl or aryl, with the proviso that when the dye contains two borin nuclei, Q has the same significance in each nuclei, and 50
 Z₁ stands for the atoms necessary to close a naphthalene nucleus or a substituted naphthalene nucleus,
 each of L₁, L₂ and L₃ stands for a methine group or a substituted methine group, 55
 R₁ stands for a saturated or unsaturated aliphatic or cycloaliphatic group or an aromatic group e.g. alkyl or substituted alkyl, cycloalkyl, allyl, aralkyl or substituted aralkyl, aryl or substituted aryl, 60
 n stands for 1 or 2,
 m stands for 1, 2 or 3,
 Z₂ stands for the atoms necessary to close a naphthalene nucleus or a substituted naphthalene nucleus, and 65
 Z₃ stands for the non-metallic atoms necessary to complete a heterocyclic nitrogen containing nucleus e.g. those of the thiazole series, those of the benzothiazole

- series e.g. benzothiazole, 5-methylbenzothiazole, 5-methoxybenzothiazole, those of the naphthothiazole series, those of the oxazole series, those of the benzoxazole series, e.g. benzoxazole, 5-methylbenzoxazole, 5,6-dimethylbenzoxazole, those of the selenazole series, those of the benzoselenazole series, those of the naphthoselenazole series, those of the benzimidazole series, e.g. 1-ethyl-5,6-dichlorobenzimidazole, 1-ethyl-5-cyanobenzimidazole, those of the thiazoline series, those of the pyrroline series, those of the 2-quinoline series, those of the 4-quinoline series and those of the 3,3-dialkylindolenine series, and

M^+ stands for a cation e.g. a proton, a metal cation or an onium cation of organic or inorganic nature.

- 20 The present invention further provides merocyanine dyes as represented by the following formula III:

III.



wherein:

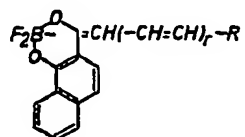
- 25 Q, L₁, L₂, L₃, Z₁, M⁺ and m have the same significance as above, and

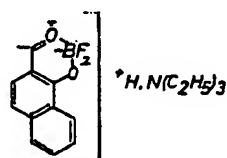
Y stands for the atoms necessary to close a heterocyclic ketomethylene nucleus e.g. those of the pyrazolone series e.g. 3-methyl-1-phenyl-5-pyrazolone; those of the isoxazolone series e.g. 3-phenyl-5-isoxazolone or 3-methyl-5-isoxazolone; those of the oxindole series; those of the 2:4:6-triketohexahydropyrimidine series, e.g. barbituric acid or 2-thiobarbituric acid or their derivatives such as those substituted in the 1-position and/or 3-position by an alkyl group or an aryl group; those of the rhodanine series (i.e. 2-thio-2:4-thiazolidinedione series), e.g. rhodanine and 3-ethylrhodanine, those of the 2-thio-2:4-oxazolidinedione series; those of the 2-thio-2:5-thiazolidinedione series; those of the 2:4-thiazolidinedione series; those of the 2-imino-4-oxazolidinone (i.e. pseudohydantoin) series; those of the 2:4-imidazolidinedione (hydantoin) series; those of the 2-thio-2:4-imidazolidinedione (i.e. 2-thiohydantoin) series.

By appropriate choice of the substituents and methine chain length, the characteristics of the sensitizers of the invention as regards sensitizing range, solubility, etc. can be adapted to the necessities.

Representative examples of dyes corresponding to the above general formulae are given in Tables I to V.

TABLE I



Dye	R	r
1	3-methylbenzothiazolium	0
2	1,3-dimethyl-5-cyanobenzimidazolium	0
3	3-ethylbenzothiazolium	1
4	3-ethylbenzoselenazolium	1
5	3-ethyl-5-methyl-benzoxazolium	1
6	3-ethylthiazolinium	1
7		1
8	idem	2

$$\text{F}_2\text{B}-\text{O}-\text{CH}=\text{CH}-\text{CH}=\text{CH})_r-\text{R}$$
INSDOCID: <GB__1353805A_I_>

c1ccc(cc1)N2C(=O)C(=O)C3=CC=CC=C3C2=C4C=CC=CC=C4C=C5C=CC=CC=C5C=C6C=CC=CC=C6C=C7C=CC=CC=C7C=C8C=CC=CC=C8C=C9C=CC=CC=C9C=C10C=CC=CC=C10C=C11C=CC=CC=C11C=C12C=CC=CC=C12C=C13C=CC=CC=C13C=C14C=CC=CC=C14C=C15C=CC=CC=C15C=C16C=CC=CC=C16C=C17C=CC=CC=C17C=C18C=CC=CC=C18C=C19C=CC=CC=C19C=C20C=CC=CC=C20C=C21C=CC=CC=C21C=C22C=CC=CC=C22C=C23C=CC=CC=C23C=C24C=CC=CC=C24C=C25C=CC=CC=C25C=C26C=CC=CC=C26C=C27C=CC=CC=C27C=C28C=CC=CC=C28C=C29C=CC=CC=C29C=C30C=CC=CC=C30C=C31C=CC=CC=C31C=C32C=CC=CC=C32C=C33C=CC=CC=C33C=C34C=CC=CC=C34C=C35C=CC=CC=C35C=C36C=CC=CC=C36C=C37C=CC=CC=C37C=C38C=CC=CC=C38C=C39C=CC=CC=C39C=C40C=CC=CC=C40C=C41C=CC=CC=C41C=C42C=CC=CC=C42C=C43C=CC=CC=C43C=C44C=CC=CC=C44C=C45C=CC=CC=C45C=C46C=CC=CC=C46C=C47C=CC=CC=C47C=C48C=CC=CC=C48C=C49C=CC=CC=C49C=C50C=CC=CC=C50C=C51C=CC=CC=C51C=C52C=CC=CC=C52C=C53C=CC=CC=C53C=C54C=CC=CC=C54C=C55C=CC=CC=C55C=C56C=CC=CC=C56C=C57C=CC=CC=C57C=C58C=CC=CC=C58C=C59C=CC=CC=C59C=C60C=CC=CC=C60C=C61C=CC=CC=C61C=C62C=CC=CC=C62C=C63C=CC=CC=C63C=C64C=CC=CC=C64C=C65C=CC=CC=C65C=C66C=CC=CC=C66C=C67C=CC=CC=C67C=C68C=CC=CC=C68C=C69C=CC=CC=C69C=C70C=CC=CC=C70C=C71C=CC=CC=C71C=C72C=CC=CC=C72C=C73C=CC=CC=C73C=C74C=CC=CC=C74C=C75C=CC=CC=C75C=C76C=CC=CC=C76C=C77C=CC=CC=C77C=C78C=CC=CC=C78C=C79C=CC=CC=C79C=C80C=CC=CC=C80C=C81C=CC=CC=C81C=C82C=CC=CC=C82C=C83C=CC=CC=C83C=C84C=CC=CC=C84C=C85C=CC=CC=C85C=C86C=CC=CC=C86C=C87C=CC=CC=C87C=C88C=CC=CC=C88C=C89C=CC=CC=C89C=C90C=CC=CC=C90C=C91C=CC=CC=C91C=C92C=CC=CC=C92C=C93C=CC=CC=C93C=C94C=CC=CC=C94C=C95C=CC=CC=C95C=C96C=CC=CC=C96C=C97C=CC=CC=C97C=C98C=CC=CC=C98C=C99C=CC=CC=C99C=C100C=CC=CC=C100C=C101C=CC=CC=C101C=C102C=CC=CC=C102C=C103C=CC=CC=C103C=C104C=CC=CC=C104C=C105C=CC=CC=C105C=C106C=CC=CC=C106C=C107C=CC=CC=C107C=C108C=CC=CC=C108C=C109C=CC=CC=C109C=C110C=CC=CC=C110C=C111C=CC=CC=C111C=C112C=CC=CC=C112C=C113C=CC=CC=C113C=C114C=CC=CC=C114C=C115C=CC=CC=C115C=C116C=CC=CC=C116C=C117C=CC=CC=C117C=C118C=CC=CC=C118C=C119C=CC=CC=C119C=C120C=CC=CC=C120C=C121C=CC=CC=C121C=C122C=CC=CC=C122C=C123C=CC=CC=C123C=C124C=CC=CC=C124C=C125C=CC=CC=C125C=C126C=CC=CC=C126C=C127C=CC=CC=C127C=C128C=CC=CC=C128C=C129C=CC=CC=C129C=C130C=CC=CC=C130C=C131C=CC=CC=C131C=C132C=CC=CC=C132C=C133C=CC=CC=C133C=C134C=CC=CC=C134C=C135C=CC=CC=C135C=C136C=CC=CC=C136C=C137C=CC=CC=C137C=C138C=CC=CC=C138C=C139C=CC=CC=C139C=C140C=CC=CC=C140C=C141C=CC=CC=C141C=C142C=CC=CC=C142C=C143C=CC=CC=C143C=C144C=CC=CC=C144C=C145C=CC=CC=C145C=C146C=CC=CC=C146C=C147C=CC=CC=C147C=C148C=CC=CC=C148C=C149C=CC=CC=C149C=C150C=CC=CC=C150C=C151C=CC=CC=C151C=C152C=CC=CC=C152C=C153C=CC=CC=C153C=C154C=CC=CC=C154C=C155C=CC=CC=C155C=C156C=CC=CC=C156C=C157C=CC=CC=C157C=C158C=CC=CC=C158C=C159C=CC=CC=C159C=C160C=CC=CC=C160C=C161C=CC=CC=C161C=C162C=CC=CC=C162C=C163C=CC=CC=C163C=C164C=CC=CC=C164C=C165C=CC=CC=C165C=C166C=CC=CC=C166C=C167C=CC=CC=C167C=C168C=CC=CC=C168C=C169C=CC=CC=C169C=C170C=CC=CC=C170C=C171C=CC=CC=C171C=C172C=CC=CC=C172C=C173C=CC=CC=C173C=C174C=CC=CC=C174C=C175C=CC=CC=C175C=C176C=CC=CC=C176C=C177C=CC=CC=C177C=C178C=CC=CC=C178C=C179C=CC=CC=C179C=C180C=CC=CC=C180C=C181C=CC=CC=C181C=C182C=CC=CC=C182C=C183C=CC=CC=C183C=C184C=CC=CC=C184C=C185C=CC=CC=C185C=C186C=CC=CC=C186C=C187C=CC=CC=C187C=C188C=CC=CC=C188C=C189C=CC=CC=C189C=C190C=CC=CC=C190C=C191C=CC=CC=C191C=C192C=CC=CC=C192C=C193C=CC=CC=C193C=C194C=CC=CC=C194C=C195C=CC=CC=C195C=C196C=CC=CC=C196C=C197C=CC=CC=C197C=C198C=CC=CC=C198C=C199C=CC=CC=C199C=C200C=CC=CC=C200C=C201C=CC=CC=C201C=C202C=CC=CC=C202C=C203C=CC=CC=C203C=C204C=CC=CC=C204C=C205C=CC=CC=C205C=C206C=CC=CC=C206C=C207C=CC=CC=C207C=C208C=CC=CC=C208C=C209C=CC=CC=C209C=C210C=CC=CC=C210C=C211C=CC=CC=C211C=C212C=CC=CC=C212C=C213C=CC=CC=C213C=C214C=CC=CC=C214C=C215C=CC=CC=C215C=C216C=CC=CC=C216C=C217C=CC=CC=C217C=C218C=CC=CC=C218C=C219C=CC=CC=C219C=C220C=CC=CC=C220C=C221C=CC=CC=C221C=C222C=CC=CC=C222C=C223C=CC=CC=C223C=C224C=CC=CC=C224C=C225C=CC=CC=C225C=C226C=CC=CC=C226C=C227C=CC=CC=C227C=C228C=CC=CC=C228C=C229C=CC=CC=C229C=C230C=CC=CC=C230C=C231C=CC=CC=C231C=C232C=CC=CC=C232C=C233C=CC=CC=C233C=C234C=CC=CC=C234C=C235C=CC=CC=C235C=C236C=CC=CC=C236C=C237C=CC=CC=C237C=C238C=CC=CC=C238C=C239C=CC=CC=C239C=C240C=CC=CC=C240C=C241C=CC=CC=C241C=C242C=CC=CC=C242C=C243C=CC=CC=C243C=C244C=CC=CC=C244C=C245C=CC=CC=C245C=C246C=CC=CC=C246C=C247C=CC=CC=C247C=C248C=CC=CC=C248C=C249C=CC=CC=C249C=C250C=CC=CC=C250C=C251C=CC=CC=C251C=C252C=CC=CC=C252C=C253C=CC=CC=C253C=C254C=CC=CC=C254C=C255C=CC=CC=C255C=C256C=CC=CC=C256C=C257C=CC=CC=C257C=C258C=CC=CC=C258C=C259C=CC=CC=C259C=C260C=CC=CC=C260C=C261C=CC=CC=C261C=C262C=CC=CC=C262C=C263C=CC=CC=C263C=C264C=CC=CC=C264C=C265C=CC=CC=C265C=C266C=CC=CC=C266C=C267C=CC=CC=C267C=C268C=CC=CC=C268C=C269C=CC=CC=C269C=C270C=CC=CC=C270C=C271C=CC=CC=C271C=C272C=CC=CC=C272C=C273C=CC=CC=C273C=C274C=CC=CC=C274C=C275C=CC=CC=C275C=C276C=CC=CC=C276C=C277C=CC=CC=C277C=C278C=CC=CC=C278C=C279C=CC=CC=C279C=C280C=CC=CC=C280C=C281C=CC=CC=C281C=C282C=CC=CC=C282C=C283C=CC=CC=C283C=C284C=CC=CC=C284C=C285C=CC=CC=C285C=C286C=CC=CC=C286C=C287C=CC=CC=C287C=C288C=CC=CC=C288C=C289C=CC=CC=C289C=C290C=CC=CC=C290C=C2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Dye	R
19	3-ethylbenzothiazolium
20	3-ethyl-5,6-dimethylbenzoxazolium
21	3-ethyl-5,6-dichlorobenzimidazolium

c1ccc(cc1)N2C(=C(R)C=C2C3C4C=CC=CC=C4OC(F)(F)F)C5C=CC=CC=C35

Dye	R
22	3-ethylbenzoselenazolium
23	1,3-diethyl-5,6-dichlorobenzimidazolium

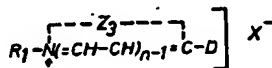
$$\left[\text{BF}_2 \text{O} \text{CH}_2 \text{CH} = \text{CH} \text{CH} \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} \begin{array}{c} \text{H} \\ \parallel \\ \text{O} \end{array} \right]^+ \text{H.N(C}_2\text{H}_5)_5$$

IV

COC1C(CF3)OCC(F)O1

These compounds can be prepared as de-

The novel cyanine dyes according to the present invention can be prepared by condensing an intermediate compound of the above formula IV with a compound of the following formula V or VI:


$$R_1 - \overset{\text{---Z---}}{\underset{\text{---}}{\text{N}}} - \text{CH}=\text{CH})_{n-1} - \text{C}(=\text{L}_1 - \text{L}_2)_{m-1} = \text{V}$$

R_1, L_1, L_2, Z_3 and n have the same significance as above.

X⁻ stands for an anion such as chloride,

bromide, iodide, perchlorate, benzene sulphonate, p-tolusulphonate, methyl sulphate, ethyl sulphate, propyl sulphate, etc. or is not present when the anion is already contained in R_1 .

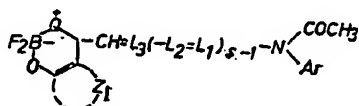
- 5 q is 2 or 3,
 D stands for alkylmercapto, arylmercapto, β -arylamino vinyl, δ -arylamino-1,3-butadienyl, β -alkylmercaptovinyl, β -arylmercaptovinyl, β -acetarylido vinyl or β -p-tolusulphoarylido vinyl, β -chlorovinyl, β -alkoxyvinyl, which vinyl groups may carry a substituent.

- 10 V stands for O, S, Se or N- R_2 , wherein R_2 is an aryl group.

The condensations are advantageously carried out in the presence of an acid anhydride such as acetic anhydride, a basic condensing agent, for example a trialkylamine such as triethylamine, a dialkylaniline or a heterocyclic tertiary amine such as pyridine or N-alkylpiperidine, and an inert diluent such as methanol, ethanol, methoxyethanol, acetone, acetonitrile, dimethylsulphoxide, etc.

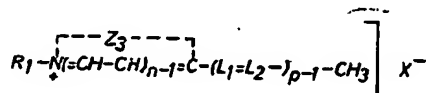
- 25 The novel cyanine dyes according to the present invention can also be prepared by condensing acetarylido intermediates represented by the following formula:

VII



- 30 wherein:
 L_1, L_2, L_3, Q, Z_1 have the same significance as above, and S is 1, 2 or 3,
 and
 Ar stand for aryl,
 35 with a compound of the formula V or of the following formula VIII:

VIII

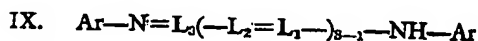


wherein:

- 40 R_1, Z_1, n and X have the same significance as above, and
 p stands for 1 when S is 3 or is 1 or 2 when S is 1 or 2.

- 45 These condensations too are advantageously carried out in the presence of a basic condensing agent and of an inert diluent as set forth above.

- 50 The acetarylido intermediates represented by formula VII above can be prepared by condensing an intermediate compound of formula IV with a compound represented by the formula IX:



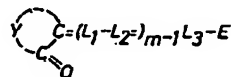
wherein:

Ar, L_1, L_2, L_3 and s have the same significance as above, and by heating the arylaminovinyl intermediates or vinylenes homologues thereof obtained, with acetic anhydride.

The symmetrical cyanine dyes of the present invention can also be obtained by condensing an intermediate compound represented by formula IV with a compound known to those skilled in the art as a compound suitable to introduce a methine group or a polymethine chain, such as an ortho carboxylic acid alkyl ester, e.g. ethyl orthoformate, an orthothiocarboxylic acid alkyl ester, an amidine, a malonaldehyde dianil, a malonaldehyde diacetal, an alkoxy acroleine acetal, a glutazonaldehyde dianil, etc.

The novel merocyanine dyes according to the present invention can be prepared by condensing an intermediate compound as represented by formula IV with a heterocyclic compound represented by the following formula X:

X



wherein:

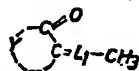
Y, L_1, L_2, L_3 and m have the same significance as above, and

E stands for a halogenation atom such as chlorine, bromine and iodine, an alkyl- or arylmercapto group, an alkoxy group, an arylamino group, an acetarylido group, a p-tolusulpharyldo group, etc.

The new merocyanine dyes can also be prepared by condensing acetarylido intermediates represented by the formula VII with compounds represented by the following formulae XIa and XIb:

XIa.

XIb.

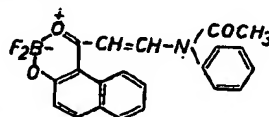


wherein:

Y and L_1 have the same significance as above.

The following preparations illustrate the preparation of intermediates for synthesizing dyes according to the present invention and the preparation of the dyes themselves.

Preparation 1



Diphenylformamidine (11.8 g; 0.06 mole), 2,2-difluoro-4-methylnaphtho[1,2-c]-1,3,2-dioxaborin (7.0 g; 0.03 mole) and acetic anhydride (20 ml) were heated to 80°C. and then left at ambient temperature for

- 1 hour. After chilling, the product was sucked off, washed with acetic anhydride and ether-acetone (1:1).
Yield: 8.4 g.
- 5 Melting point: 240—242° C.
The isomer 2,2 - difluoro - 4 - (2 - acetanilidovinyl)naphtho[2,1 - e] - 1,3,2 - dioxaborin can be prepared in a similar way.
- Preparation 2 (Dye 1)*
10 A mixture of 2 - methylthio - 3 - methylbenzothiazolium p-tolusulphonate (1.83 g; 0.005 mole), 2,2 - difluoro - 4 - methyl-naphtho[2,1 - e] - 1,3,2 - dioxaborin (1.17 g; 0.005 mole), acetonitrile (40 ml) and triethylamine (1.4 ml; 0.1 mole) was kept at room temperature for 1 hour. The dye formed was collected by filtration and digested with 50 ml of hot methanol.
Yield: 0.9 g.
20 Melting point: above 260° C.
Absorption maxima (measured in dimethylsulphoxide):
454 nm; $\epsilon = 5.9 \times 10^4$
430 nm; $\epsilon = 5.3 \times 10^4$
- 25 Dye 9 can be prepared in a similar way.
- Preparation 3 (Dye 2)*
A mixture of 2 - methylthio - 1,3 - methyl-5 - cyanobenzimidazolium methylsulphate (1.65 g; 0.005 mole), 2,2 - difluoro - 4 - methyl-naphtho[2,1 - e] - 1,3,2 - dioxaborin (1.17 g; 0.005 mole), acetonitrile (25 ml) and triethylamine (1.4 ml; 0.01 mole) were heated to the boiling point, then left for 15 minutes and cooled externally with tap water. The precipitated dye was collected by filtering with suction and then washed with acetonitrile and methanol.
Yield: 0.7 g.
Melting point: above 260° C.
40 Absorption maximum: (measured in dimethylsulphoxide): 400 nm; $\epsilon = 3.9 \times 10^4$.
- Preparation 4 (Dye 3)*
A solution of 2 - phenyliminoethylidene-3 - ethyl - 2,3 - dihydrobenzothiazole (1.4 g; 0.005 mole) in acetonitrile (25 ml) was mixed with a solution of 2,2 - difluoro - 4 - methyl-naphtho[2,1 - e] - 1,3,2 - dioxaborin (1.17 g; 0.005 mole) in acetonitrile (25 ml). Acetic anhydride (1.1 ml; 0.01 mole) and triethylamine (1.4 ml; 0.01 mole) were added and the mixture was kept for 30 minutes at ambient temperature. The precipitated dye was filtered off, boiled with methanol (30 ml), filtered off with suction and washed with methanol.
Yield: 1 g.
55 Melting point: above 270° C.
Abs. max. (measured in dimethylsulphoxide):
574 nm; $\epsilon = 1.26 \times 10^5$
60 535 nm; $\epsilon = 0.73 \times 10^5$
- Dyes 4, 11, 21, 23 can be prepared in a similar way.
- Preparation 5 (Dye 10)*
To a mixture of 2,2 - difluoro - 4 - methyl-naphtho[1,2 - e] - 1,3,2 - dioxaborin (2.34 g; 0.01 mole), acetonitrile (40 ml), acetic anhydride (1.1 ml; 0.01 mole) and triethylamine (1.4 ml; 0.01 mole) at ambient temperature, 2 - phenyliminoethylidene - 3 - ethyl - 2,3 - dihydrobenzothiazole (2.8 g; 0.01 mole) was added portion-wise. After 30 minutes the dye was collected and washed with acetonitrile and ether.
Yield: 1.2 g.
Melting point: 270° C.
75 Abs.max (measured in dimethylsulphoxide):
590 nm; $\epsilon = 7.7 \times 10^4$
552 nm; $\epsilon = 6.7 \times 10^4$.
- Preparation 6 (Dye 5)*
A solution of 2 - phenyliminoethylidene-3 - ethyl - 5 - methyl - 2,3 - dihydrobenzoxazole (1.8 g; 0.005 mole) in acetonitrile (25 ml) and a solution of 2,2 - difluoro - 4 - methyl-naphtho[2,1 - e] - 1,3,2 - dioxaborin (1.17 g; 0.005 mole) were mixed and acetic anhydride (0.6 ml) was then added. After 1 hour the precipitated dye was collected, washed with acetonitrile, boiled with dimethylformamide, filtered off and washed with ethanol and ether.
Yield: 0.8 g.
Melting point: above 270° C.
Abs.max. (measured in dimethylformamide):
550 nm; $\epsilon = 1.07 \times 10^5$
511 nm; $\epsilon = 0.83 \times 10^5$. 95
- Preparation 7 (Dye 6)*
A solution of 2 - (2 - acetanilidovinyl) - 3 - ethylthiazolium bromide (1.77 g; 0.005 mole) in methoxyethanol (25 ml) was mixed with a solution of 2,2 - difluoro - 4 - methyl-naphtho[2,1 - e] - 1,3,2 - dioxaborin (1.11 g; 0.005 mole) in acetonitrile whereupon acetic anhydride (0.6 ml) and triethylamine (0.7 ml) were added. After 30 minutes the dye was collected and recrystallized once from dimethylformamide - ethanol and once from acetone.
Yield: 0.35 g.
Melting point: above 270° C.
Abs.max. (measured in methanol): 110
518; $\epsilon = 1.08 \times 10^5$
486; $\epsilon = 0.70 \times 10^5$
- Dye 13 can be prepared in a similar way.
- Preparation 8 (Dye 14)*
To 1 - ethyl - 2(2 - anilino vinyl) - pyrrolinium iodide (3.42 g; 0.01 mole) and 2,2 - difluoro - 4 - methyl-naphtho[1,2 - e] - 1,3,2 - dioxaborin (2.34 g; 0.01 mole) in acetonitrile 115

- (30 mole), acetic anhydride (2 ml) and triethylamine (1.4 ml) were added. The mixture was left standing overnight. The precipitate was collected and washed with acetonitrile and ether.
- Yield: 0.9 g.
Melting point: 260° C. (Decomposition).
Abs.max. (measured in dimethylsulphoxide):
- 516 nm; $\epsilon=4.1 \times 10^4$
495 nm; $\epsilon=4.9 \times 10^4$
- Preparation 9 (Dye 12)**
A mixture of anhydro - 2 - methyl - 3 - (3-sulphatopropyl)benzothiazolium hydroxide (1.94 g; 0.005 mole), 2,2 - difluoro - 4 - (2-acetanilidovinyl) naphtho[1,2 - e] - 1,3,2-dioxaborin (1.9 g; 0.005 mole), acetonitrile (20 ml), acetic anhydride (1 ml) and triethylamine (1.4 ml) was stirred for 30 minutes at ambient temperature. The dye formed was sucked off, dissolved in a mixture of ethanol and dimethylformamide (4:1), filtered from some colourless material and brought to crystallization by the addition of ether.
- Yield: 1 g.
Melting point: 200° C. Decomposition.
Abs.max. (measured in methanol):
- 584 nm; $\epsilon=4.7 \times 10^4$
545 nm; $\epsilon=3.9 \times 10^4$
- Preparation 10 (Dye 7)**
A mixture of 2,2 - difluoro - 4 - (2-acetanilidovinyl) naphtho[2,1 - e] - 1,3,2-dioxaborin (1.9 g; 0.005 mole), 2,2 - difluoro - 4 - methyl-naphtho[2,1 - e] - 1,3,2-dioxaborin (1.17 g; 0.005 mole), acetonitrile (25 ml), acetic anhydride (1 ml) and triethylamine (1.4 ml) was heated to 40° C. After 30 minutes, isopropanol (50 ml) was added and the mixture chilled. The precipitate was collected and washed with isopropanol.
- Yield: 2.0 g.
Melting point: 240—250° C. Decomposition.
Abs.max. (measured in methanol):
- 581; $\epsilon=2.07 \times 10^5$
540; $\epsilon=0.70 \times 10^6$
- Dye 16 can be prepared in a similar way.
- Preparation 11 (Dye 8)**
A mixture of 2,2 - difluoro - 4 - methyl-naphtho[2,1 - e] - 1,3,2 - dioxaborin (2.34 g; 0.01 mole), malonaldehyde dianil hydrochloride (1.3 g; 0.005 mole), acetonitrile (30 ml), acetic anhydride (2 ml) and triethylamine (1.4 ml) was refluxed for 15 minutes, cooled, diluted with ether (100 ml) and left standing overnight. The dye obtained was boiled with ethanol, collected by filtration and washed with ethanol.
- Yield: 1.25 g.
Melting point: 252—255° C.
Abs.max. (measured in dimethylsulphoxide):
- 677 nm; $\epsilon=1.87 \times 10^5$
625 nm; $\epsilon=0.63 \times 10^5$
- Preparation 12 (Dye 17)**
A mixture of 2,2 - difluoro - 4 - (2-acetanilidovinyl) naphtho [1,2 - e] - 1,3,2 - dioxaborin (1.9 g; 0.005 mole), 2 - (2-methoxypropenyl) - 3 - ethylbenzothiazolium-methylsulphate (1.72 g; 0.005 mole), acetonitrile (20 ml), triethylamine (1.4 ml) and acetic anhydride (1 ml) was kept for 30 minutes, at ambient temperature. The dye was collected by filtration, washed with acetonitrile, boiled with methanol (50 ml) and filtered whilst hot.
- Yield: 1.8 g.
Melting point: above 260° C.
Abs.max. (measured in dichloroethane):
- 650 nm; $\epsilon=1.08 \times 10^5$
- Preparation 13 (Dye 18)**
A mixture of 2,2 - difluoro - 4 - (2-acetanilidovinyl) naphtho [1,2 - e] - 1,3,2 - dioxaborin (1.7 g; 0.0045 mole), 2 - (2-methylthiopropenyl) - 3 - ethylbenzothiazolium methylsulphate (1.62 g; 0.0045 mole), acetonitrile (20 ml), acetic anhydride (0.5 ml) and triethylamine (1.4 ml) was refluxed for 5 minutes. After cooling, the dye was collected and recrystallized from dimethylformamide-methanol.
- Yield: 1.4 g.
Melting point: 260° C. Decomposition.
Abs.max. (measured in dichloroethane):
- 684 nm; $\epsilon=9.4 \times 10^4$.
- Preparation 14 (Dye 19)**
A mixture of 2 - phenyliminoethylidene - 3-ethyl - 2,3 - dihydrobenzothiazole (2.8 g; 0.01 mole), 2,2 - difluoro - 3 - phenyl - 4 - methyl-naphtho [2,1-e]-1,3,2-oxazaborin (3.1 g; 0.01 mole), acetonitrile (25 ml), acetic anhydride (1.1 ml) and triethylamine (1.4 ml) was refluxed for 5 minutes. The dye that crystallised on cooling, was collected and boiled out with acetone (50 ml).
- Yield: 3.9 g.
Melting point: above 260° C.
Abs.max. (measured in dimethylsulphoxide):
- 528 nm; $\epsilon=5.3 \times 10^4$.
- Dye 22 can be prepared in a similar way.
- Preparation 15 (Dye 20)**
2,2 - difluoro - 3 - phenyl - 4 - methyl-naphtho[2,1 - e] - 1,3,2 - oxazaborin (1.55 g; 0.005 mole) and 2-phenyliminoethylidene - 3-

ethyl - 5,6 - dimethyl - 2,3 - dihydrobenzoxazole were dissolved in dimethylsulphoxide (20 ml) by heating at 60° C. After cooling to room temperature, a mixture of triethylamine (0.7 ml) and acetic anhydride (0.6 ml) was added. After heating for 10 minutes at 60° C., the reaction mixture was poured into isopropanol (100 ml) whereupon the dye crystallised. It was boiled out with methanol (50 ml) and filtered whilst hot.

Yield: 1.5 g.

Melting point: above 270° C.

Abs.max. (measured in dimethylsulphoxide):

515 nm; $\epsilon = 6.3 \times 10^4$

15 Dye 15 can be prepared in a similar way.

Preparation 16 (Dye 24)

Barbituric acid (1.28 g; 0.01 mole), 2,2-difluoro - 4 - (2 - acetanilidovinyl) - naphtho[1,2 - c] - 1,3,2 - dioxazaborin (3.8 g; 0.01 mole), acetonitrile (60 ml), triethylamine (2.8 ml) and acetic anhydride (1.1 ml) were refluxed for 15 minutes. The dye that crystallised on cooling, was collected and boiled out with methanol (100 ml).

25 Yield: 3.1 g.

Melting point: above 260° C.

Abs.max. (measured in methanol):

508 nm; $\epsilon = 5.9 \times 10^4$

480 nm; $\epsilon = 4.1 \times 10^4$

30 The dyes according to the present invention are particularly useful for spectrally sensitizing a photo-conductive substance e.g. an inorganic photoconductive compound for instance photoconductive zinc oxide dispersed in a binder.

35 Thus the invention also provides photoconductive recording material comprising a photoconductive substance wherein the said substance is spectrally sensitized by means of the novel cyanine or merocyanine dyes hereinbefore set forth.

40 The sensitizing dyes used in the present invention can be allowed to absorb to the inorganic photoconductive substance, preferably photoconductive zinc oxide, by adding them to a dispersion of that substance in an organic or aqueous medium either or not already containing the binder. In particular, a photoconductive layer of a recording material may contain the photoconductive zinc oxide dispersed in a binder, which during the coating step was dissolved in an aqueous alkaline medium.

50 Zinc oxide recording layers applied from organic solvents and binding agents soluble in the organic medium are described e.g. in the Belgian Patent Specifications 612,102 and 714,257.

55 Zinc oxide recording layers applied from an aqueous medium are described in the

United Kingdom Patent Specifications 1,125,579 and 1,125,580.

The spectral sensitizing agents are preferably added in dissolved state, e.g. dissolved in a water-miscible solvent or in water, to a dispersion of the photoconductive zinc oxide. When applied in an aqueous zinc oxide dispersion they are preferably incorporated into the recording layer from an organic liquid consisting of or containing a solvent, preferably which has a very low vapour pressure and which is at least for 20% by weight soluble in water at 20° C. Examples of such a solvent are methanol, ethanol and dimethylformamide. Such a method for sensitizing a photoconductive material is described in the United Kingdom Patent Specification 1,154,613 which should be read in conjunction herewith.

Suitable dispersing agents for dispersing photoconductive zinc oxide in an aqueous medium are described in the French Patent Specification 1,540,020 which should also be read in conjunction herewith.

The optimum quantity of sensitizing agent per gram of photoconductive zinc oxide can be determined easily by a series of tests. A useful range is comprised between 0.01 mg and 5 mg per gram of photoconductive zinc oxide. The weight ratio of zinc oxide to binder may vary between relatively large limits. A ratio of 1 part by weight of photoconductive substance to 0.1 to 0.6 part by weight of total content of binder is preferred. Advantageously the coating mixture contains dispersed photoconductive zinc oxide in a weight ratio of 95% to 60% in respect of the total solids content of the coated and dried layer. The thickness of the photoconductive layer may be chosen between wide limits according to the requirements of each case. Good recording and reproduction results are attained with electrophotographic layers having a thickness of 1 to 20 μ , and preferably of 3 to 10 μ .

105 Preferably the sensitizing substances are used in combination with photoconductive zinc oxide prepared according to the French process.

The photoconductive recording layers containing a spectral sensitizing agent as described above may contain, in addition to the photoconductive substance(s) and the binder, spectral sensitizers of any other type (see e.g. United Kingdom Patent Specification 1,020,504), compounds increasing the dark-resistivity e.g. the phosphorus compounds described in the Belgian Patent Specification 612,102, and additives known in coating techniques e.g. pigments (see e.g. United Kingdom Patent Specification 1,007,349), compounds influencing the gloss and/or the viscosity, and compounds that counteract aging and/or oxidation of the layers, or which in-

fluence the thermal stability of the layers. When selecting any additives, preference is given to those which least reduce the dark-resistivity of the photoconductive layer.

5 The photoconductive composition sensitized according to the present invention may be coated on a support according to a known coating technique, e.g. by spraying, whirling, dip-coating, or by a coating technique where-
10 in use is made of a doctor blade. The supports or base materials are chosen in view of the particular charging, exposure, recording, development and/or transfer technique wherein the recording material is used.

15 In electrophotographic recording techniques, wherein the photoconductive layer is electrostatically charged, the support preferably has an electric volume resistivity, which is considerably lower than that of the recording layer. Suitable supports are described e.g.
20 in the United Kingdom Patent Specifications 995,491, 1,020,503, and 1,020,504, and in the United States Patent Specification 3,008,825.

The photoconductive layer of an electro-
25 photographic material, which is prepared starting from a coating composition according to the present invention, can be used for recording purposes, in which prior to exposure an electric charge is non-differentially applied
30 according to known methods. However, the material can also be used in recording techniques, in which the exposure step precedes the charging step. For such a technique we may refer to e.g. United Kingdom Patent
35 Specifications 1,033,419 and 1,033,420.

For comparison of the sensitivity of photo-
conductive recording elements, said elements
are exposed in the same manner, e.g. through
40 a step-wedge, and developed in the same conditions. Well established methods of developing electrostatic images include cascade-,
powder cloud-, magnetic brush- and fur-brush-
development. These methods are based on
the application of charged dry toner to the
45 surface bearing the electrostatic image. Other methods are based on the use of liquids, either insulating (electrophoretic development) or
conductive liquids (see e.g. the United States
Patent Specification 2,907,674 and the Bel-
50 gian Patent Specifications 610,060 and 625,335). Development of a conductivity

image based on electrolysis is described e.g. by J. A. Amick, R.C.A. Rev., 20, 753 (1959).

The following example illustrates the present invention.

Example.

A mixture is made of:			
photoconductive zinc oxide	20	g	60
1,2-dichloroethane	27	g	
ethyl acetate	8.8	g	
10% solution of tetrachlorophthalic anhydride in ethanol	0.66	ml	65
20% solution of co(vinyl chloride/vinylidene chloride/maleic anhydride/acrylonitrile) (% by weight: 57/40/2/1) in 1,2-dichloroethane/ethyl acetate (vol. % 1:1)	2.4	g	
50% solution of co(vinyl acetate/ethyl acrylate/acrylic acid) (% by weight: 87/12/1) in a mixture of toluene, 1,2-dichloroethane and ethyl acetate (vol. % 1:1:4)	2	g	

The composition obtained is sensitized by means of one of the sensitizing dyes listed in the following table. Each sensitizing dye is added in an amount of 0.5 mg per gram of zinc oxide in the form of a 0.1% solution in dimethylformamide and is intimately mixed with the ground composition.

Each sensitized composition is coated pro rata of 25 g of zinc oxide per sq.m on a baryta paper weighing 90 g/sq.m.

After having been dried, the layers obtained are charged, exposed for 15 sec. with an irradiation intensity of 2280 lux by means of an incandescent lamp of 450 watt through a step wedge having a constant 0.1.

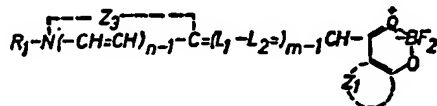
The differently sensitized layers are developed electrophoretically. The sensitivity of the obtained recording layers is expressed by the number of steps corresponding with the discharged areas on which no developing particles are deposited, which areas thus kept the original density of the recording layer. The higher this number, the more sensitive the layer.

TABLE

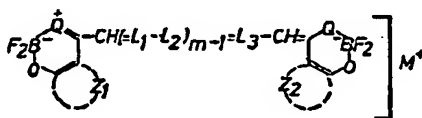
Sensitizing dye added	Sensitivity (number of non-blackened areas)	Sens. max. (nm)
—	9	—
1	13	515
3	24	575
4	24	605
5	20	555
6	21	535
7	24	592
8	21	605
10	25	605
11	14	518—598
12	26	593
13	22	535
14	20	515
15	26	516
16	17	500
17	25	654
18	24	670
19	19	538
20	16	508
21	15	532
22	17	518
23	10	468
24	24	488—518

WHAT WE CLAIM IS:—

1. A cyanine dye corresponding to one of the formulae:



5 and



wherein:

Q stands for oxygen or the group N—R
wherein R is an aliphatic cycloaliphatic
10 or aromatic group, with the proviso that
when the dye contains two boron nuclei,
Q has the same significance in each nuclei,
and

Z₁ stands for the atoms necessary to close
a naphthalene nucleus or a substituted
15 naphthalene nucleus,
each of L₁, L₂, and L₃ stands for methine
or substituted methine,

R₁ stands for a saturated or unsaturated
20 aliphatic or cycloaliphatic group or an
aromatic group,

n stands for 1 or 2,

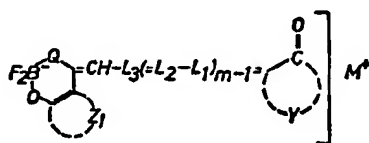
m stands for 1, 2 or 3,

Z₂ stands for the atoms necessary to close a
25 naphthalene nucleus or a substituted
naphthalene nucleus,

Z₃ stands for the non-metallic atoms neces-
sary to complete a heterocyclic nitrogen
containing nucleus, and

30 M⁺ stands for a cation.

2. A merocyanine dye corresponding to the
formula:



wherein:

35 Q stands for oxygen or the group N—R
wherein R is an aliphatic, cycloaliphatic
or aromatic group, and

Z₁ stands for the atoms necessary to close
a naphthalene nucleus or a substituted
40 naphthalene nucleus,

each of L₁, L₂, L₃ stands for methine or sub-
stituted methine,

m stands for 1, 2 or 3,

M⁺ stands for a cation, and

45 Y stands for the atoms necessary to close a
ketomethylene nucleus.

3. Method for the preparation of a cyanine

dye according to claim 1, wherein an inter-
mediate compound of the formula:



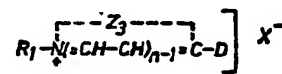
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wherein:

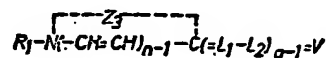
Q and Z₁ have the same significance as in
claim 1,

is condensed with a compound corresponding
to one of the formulae:

55



and



wherein:

R₁, Z₂, n, L₁ and L₂ have the same significance
as in claim 1,

X⁻ stands for an anion or is not present when
the anion is contained in R₁,

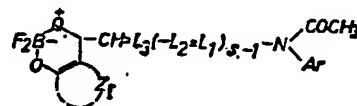
q is 2 or 3,

D stands for alkylmercapto, arylmercapto, β-
arylamino, 8-arylamino - 1,3 - buta-
dienyl, β - alkylmercaptovinyl, β - aryl-
mercaptovinyl, β-acetylarylidovinyl, β-p-
tolylsulphoarylidovinyl, β-chlorovinyl or β-
alkoxyvinyl in which all vinyl groups may
65 carry a substituent, and

V stands for oxygen, sulphur, selenium or
N(R₂) wherein R₂ is aryl.

4. Method for the preparation of a cyanine
dye according to claim 1, wherein an inter-
mediate compound of the formula:

75

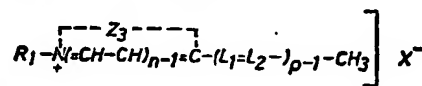


wherein:

Q, Z₁, L₁, L₂, L₃ have the same significance
as in claim 1, s is 1, 2 or 3 and Ar stands
for aryl,

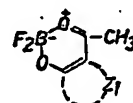
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is condensed with a compound corresponding
to one of the formulae:



and

85



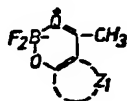
wherein:

R_1 , Z_1 , Z_2 , n , L_1 , L_2 and Q have the same significance as in claim 1,

5 X^- stands for an anion, or is not present when the anion is contained in R_1 , and

p stands for 1 when s is 3 or is 1 or 2 when s is 1 or 2.

10 5. Method for the preparation of a symmetrical cyanine dye according to claim 1, wherein an intermediate compound of the formula:

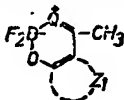


wherein:

15 Q and Z_1 have the same significance as in claim 1,

is condensed with an orthocarboxylic acid alkyl ester, an orthothiocarboxylic acid alkyl ester, an imidine, a malonaldehyde dianil, a malonaldehyde diacetal, an alkoxyacrolein acetal or a glutacetaldehyde dianil.

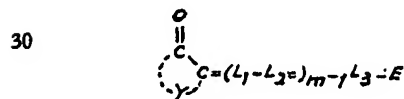
20 6. Method for the preparation of a merocyanine dye according to claim 2, wherein an intermediate of the formula:



25 wherein:

Q and Z_1 have the same significance as in claim 2,

is condensed with a heterocyclic compound of the formula:

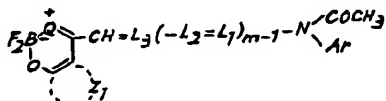


wherein:

Y , L_1 , L_2 , L_3 and m have the same significance as in claim 2, and

35 E stands for a halogen atom, an alkyl- or arylmercapto group, an alkoxy group, an arylamino group, an acetarylido group or a p-tolusulpharylido group.

7. Method for the preparation of a merocyanine dye according to claim 2, wherein an intermediate of the formula:

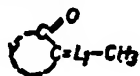


wherein:

Q , Z_1 , L_1 , L_2 , L_3 , and m have the same significance as in claim 2, and

45 Ar stands for aryl,

is condensed with a compound corresponding to one of the formulae:



and



50

wherein:

Y and L_1 have the same significance as in claim 2.

8. A photoconductive recording material comprising a photoconductive substance wherein the said substance is spectrally sensitized by means of a cyanine dye according to claim 1.

9. A photoconductive recording material comprising a photoconductive substance wherein the said substance is spectrally sensitized by means of a merocyanine dye according to claim 2.

10. A photoconductive recording material according to claim 8 or 9, wherein the photoconductive substance is an inorganic photoconductor.

11. A photoconductive recording material according to claim 10, wherein said inorganic photoconductor is zinc oxide.

12. A photoconductive recording material according to claim 10 or 11, wherein said material is prepared starting from a photoconductive composition containing water.

13. A photoconductive recording material according to claim 12, containing a photoconductive layer comprising photoconductive zinc oxide dispersed in a binder, which during the coating step was dissolved in an aqueous alkaline medium.

14. A photoconductive recording material according to claim 10 or 11, wherein the photoconductive layer is prepared according to United Kingdom Patent Specifications 1,125,579 and 1,125,580.

15. A photoconductive recording material comprising an inorganic photoconductive substance which is spectrally sensitized with a dye as defined in claim 1 or 2, which dye in the formation of the photoconductive coating has been dissolved in an organic solvent and which is at least for 20% by weight soluble in water at 20° C.

16. A photoconductive recording material according to claim 15, wherein said solvent is methanol, ethanol or dimethylformamide.

17. A photoconductive recording material containing photoconductive zinc oxide spectrally sensitized with a dye as defined in claim 1 or 2, and dispersed according to the process described in French Patent Specification 1,540,020.

18. A photoconductive recording material according to claim 8 or 9, and substantially as described herein.

5 19. A photoconductive recording material comprising photoconductive zinc oxide spectrally sensitized with one of dyes identified herein.

10 20. A process for spectrally sensitizing a photoconductive substance by allowing to adsorb thereon a dye as defined in claim 1 or 2.

15 21. A process for spectrally sensitizing a photoconductive recording material by allowing to adsorb a dye as defined in claim 1 or 2, to photoconductive zinc oxide contained in a photoconductive recording layer prepared

according to the Belgian Patent Specification 714,257.

22. A process for spectrally sensitizing a photoconductive recording material according to claim 20 and substantially as described herein. 20

23. A process for spectrally sensitizing a photoconductive recording material by allowing to adsorb to photoconductive zinc oxide one of the dyes identified herein. 25

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